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Hydrogen desorption kinetics of the destabilized LiBH₄–AlH₃ composites

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ABSTRACT

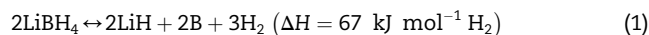
LiBH₄ can be destabilized by AlH₃ addition. In this work, the hydrogen desorption kinetics of the destabilized LiBH₄–AlH₃ composites were investigated. Isothermal hydrogen desorption studies show that the LiBH₄ + 0.5AlH₃ composite releases about 11.0 wt% of hydrogen at 450 °C for 6 h and behaves better kinetic properties than either the pure LiBH₄ or the LiBH₄ + 0.5Al composite. The apparent activation energy for the LiBH₄ decomposition in the LiBH₄ + 0.5AlH₃ composite estimated by Kissinger's method is remarkably lowered to 122.0 kJ mol⁻¹ compared with the pure LiBH₄ (169.8 kJ mol⁻¹). Besides, AlH₃ also improves the reversibility of LiBH₄ in the LiBH₄ + 0.5AlH₃ composite. For the LiBH₄ + xAlH₃ (x = 0.5, 1.0, 2.0) composites, the decomposition kinetics of LiBH₄ are enhanced as the AlH₃ content increases. The sample LiBH₄ + 2.0AlH₃ can release 82% of the hydrogen capacity of LiBH₄ in 29 min at 450 °C, while only 67% is obtained for the LiBH₄ + 0.5AlH₃ composite in 110 min. Johnson–Mehl–Avrami (JMA) kinetic studies indicate that the reaction LiBH₄ + Al → 'Li–Al–B' + AlB₂ + H₂ is controlled by the precipitation and subsequently growth of AlB₂ and Li–Al–B compounds with an increasing nucleation rate.

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Introduction

With a high hydrogen density of 18.5 wt%, lithium borohydride (LiBH₄) has draw much attention for on-board hydrogen storage during the last decade [1–14]. However, LiBH₄ is thermodynamically stable and only liberate hydrogen (Eq. (1)) at a temperature higher than 400 °C at 1 bar H₂ [1]. What's

more, the recovery of LiBH₄ following the reverse reaction of Eq. (1) requires a temperature over 600 °C and a hydrogen pressure higher than 155 bar H₂ [2].



The metallic aluminium (Al) or Al-containing compounds (e.g., LiAlH₄, Li₃AlH₆) have been employed as a destabilization

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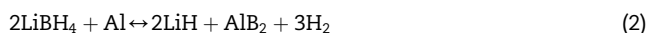
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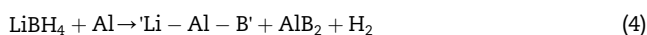
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agent to improve the hydrogen desorption/absorption properties of LiBH_4 [15–27]. The Al-containing compounds like LiAlH_4 or Li_3AlH_6 will first undergo decomposition to generate Al, which then reacts with LiBH_4 based on Eq. (2) to form AlB_2 , thus destabilize LiBH_4 . It was theoretically estimated by Cho et al. that the decomposition temperature of Eq. (2) is only 188 °C at 1 bar H_2 , which is significantly lower than that of the pure LiBH_4 (403 °C) [15].



In our previous work, aluminium hydride (AlH_3) was employed as a novel Al source to destabilize LiBH_4 [16]. It was found that AlH_3 is better as an Al source than the metallic Al. This is due to both that AlH_3 is a brittle metal hydride which can be easily refined by ball milling and that AlH_3 can generate oxide-free Al after decomposition. The hydrogen desorption process of the $\text{LiBH}_4 + 0.5\text{AlH}_3$ composite when heating from room temperature to 500 °C is composed of three steps. The first step is the self-decomposition of AlH_3 forming Al (Eq. (3)) and the second step is the subsequent decomposition of LiBH_4 reacting with Al and forming AlB_2 and Li–Al–B compounds (Eq. (4)). When the reaction Eq. (4) proceed to a certain extent, LiBH_4 will no longer react with Al due to the kinetic barrier of the formed AlB_2 and Li–Al–B layers covering the Al particle surfaces. In this case, the residual LiBH_4 tends to undergo a self-decomposition forming LiH and B and releasing hydrogen, which corresponds to the third decomposition step (Eq. (1)). However, the hydrogen desorption kinetics of the LiBH_4 – AlH_3 systems and the detailed reaction mechanism between LiBH_4 and Al are still unclear.



In the present work, in order to gain an insight into the hydrogen desorption kinetics of the LiBH_4 – AlH_3 systems and also into the kinetic model of the reaction between LiBH_4 and Al, the hydrogen desorption kinetics of the $\text{LiBH}_4 + 0.5\text{AlH}_3$ composite were first studied compared with the $\text{LiBH}_4 + 0.5\text{Al}$ composites. Then, the hydrogen desorption properties of the $\text{LiBH}_4 + x\text{AlH}_3$ ($x = 0.5, 1, 2$) composites are investigated to demonstrated the effect of AlH_3 addition of various contents on the hydrogen desorption kinetics of LiBH_4 . Finally, the kinetic model of the reaction between LiBH_4 and Al is preliminarily revealed and discussed.

Experimental details

LiBH_4 (Acros, 95%) and Al (Sinopharm Group, 99%) were used as received. AlH_3 was synthesized by a wet chemical method summarized by Brower et al. [28]. The detailed synthesis process can be found in other literatures [29–31].

The LiBH_4 , $\text{LiBH}_4 + 0.5\text{Al}$, $\text{LiBH}_4 + 0.5\text{AlH}_3$, and the $\text{LiBH}_4 + x\text{AlH}_3$ ($x = 0.5, 1, 2$) samples were prepared by ball milling using a planetary ball mill (QM-3SP4, Nanjing Nanda Instrument Plant). Experimentally, 1 g samples and 50 g stainless steel balls were sealed in a stainless steel vial with an internal volume of 100-mL in an argon-filled glovebox. The

milling process was carried out at 400 rpm for 30 min. During the milling process, it was paused every 6 min for cooling to prevent temperature rising of local areas resulting from long-term milling.

The hydrogen desorption/absorption measurements were carried out on a Sieverts-type apparatus. For the non-isothermal hydrogen desorption measurements, the samples were heated from room temperature to 500 °C with a heating rate of 4 °C min^{-1} and then kept at 500 °C for 1 h. For the isothermal hydrogen desorption measurements, the samples were rapidly heated to 450 °C and held at 450 °C. For the hydrogen absorption measurements, the dehydrogenated samples were first heated to 400 °C and hold at this temperature. Then hydrogen of about 5 MPa was filled into the sample chamber. The hydrogen absorption process proceeded for 5 h.

The thermal analysis was carried out on a differential scanning calorimeter (DSC, Netzsch STA449F3). The samples were heated from room temperature to 500 °C with a set heating rate, during which an argon atmosphere was flowed at 50 mL min^{-1} to prevent oxidation of the samples. The powder X-ray diffraction (XRD) was carried out on a PANalytical X-ray diffractometer (X'Pert Pro, Cu $K\alpha$, 40 kV, 40 mA). During the XRD measurements, the samples were sealed with an amorphous membrane to avoid oxidation. A field emission scanning electronic microscopy (SEM, FEI SIRION 100) was used to study the morphologies of the samples.

Results and discussion

The hydrogen desorption kinetics of the LiBH_4 , $\text{LiBH}_4 + 0.5\text{Al}$ and $\text{LiBH}_4 + 0.5\text{AlH}_3$ samples were first studied by isothermal hydrogen desorption measurements. The samples were rapidly heated to 450 °C and kept at 450 °C in a chamber with an initial pressure of vacuum. Fig. 1a shows the isothermal hydrogen desorption curves of the samples at 450 °C plotted as the hydrogen desorption capacity of the sample versus desorption duration, while Fig. 1b displays the hydrogen desorption extent of LiBH_4 in each sample versus desorption duration.

It can be observed from Fig. 1a that the three samples behave different decomposition process. The decomposition of the pure LiBH_4 shows an acceleration-deceleration-acceleration-deceleration process and release hydrogen of 9.8 wt%. The $\text{LiBH}_4 + 0.5\text{Al}$ composite presents a sigmoid-type process and release hydrogen of 7.0 wt%, which is lower than that of the pure LiBH_4 . This is because Al in the $\text{LiBH}_4 + 0.5\text{Al}$ composite do not contain any hydrogen. As for the $\text{LiBH}_4 + 0.5\text{AlH}_3$ composite, it can be seen that the decomposition proceed through three steps, which is very similar to the non-isothermal decomposition process reported in the previous work [16]. The first step of the isothermal decomposition of $\text{LiBH}_4 + 0.5\text{AlH}_3$ in Fig. 1a is related to the first self-decomposition of AlH_3 generating Al and releasing hydrogen of 3.5 wt% (Eq. (3)). The second decomposition step is related to the reaction between LiBH_4 and the previously formed Al forming AlB_2 and Li–Al–B compounds and releasing hydrogen of 1.4 wt% (Eq. (4)). When the reaction Eq. (4) proceeds to a certain degree, it tends to

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